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Iron(III) Complex Catalyzed Nitrosation of Terminal and 1,2-Disubstituted Olefins with Butyl Nitrite and Phenylsilane

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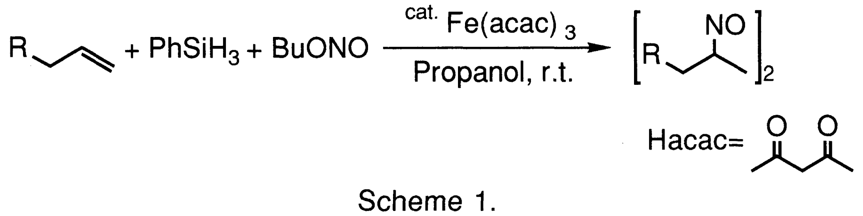
In the presence of a catalytic amount of tris(1,3-diketonato)iron(III) complex, various terminal and 1,2-disubstituted olefins are converted into the corresponding nitroso alkane dimers in fairly good yields on treatment with phenylsilane and butyl nitrite at room temperature.

Introduction of a nitrogen atom into olefinic compounds is one of the useful methods for the preparation of nitrogen-containing compounds, and the methods using a transition-metal complex as catalyst has been studied extensively in view of the utility in organic synthesis.1) For example, the conjugated olefins such as styrene were allowed to react with nitrogen monoxide or butyl nitrite in the presence of tetraethylammonium borohydride and bis(dimethylglyoximato)cobalt complex catalyst to give the corresponding oximes.2) However, the above-mentioned reaction is limited to conjugated olefins such as styrene, and no oximation and nitrosation of non-conjugated olefins catalyzed by the transition-metal complex have been known.

On the other hand, we reported the preparation of 2-nitroso amides from α,β-unsaturated amides with nitrogen monoxide and triethylsilane by using *N,N'*-bis(2-ethoxycarbonyl-3-oxobutylidene)ethylenediaminato-cobalt(II) complex (Co(eobe)) as a catalyst.3) And also, in the previous papers,4) we showed that 2-hydroxyimino carbonyl compounds such as 2-hydroxyimino esters and ketones were obtained from the corresponding α,β-unsaturated carbonyl compounds in good yields by the use of butyl nitrite as a nitrogen source instead of nitrogen monoxide. In the course of our continuing study, it was found that, when a tris(1,3-diketonato)iron(III) complex such as tris(acetylacetonato)iron(III) ($Fe(acac)_3$) was used as a catalyst, the nitrosation of terminal and 1,2-disubstituted olefins proceeded smoothly to form the corresponding nitroso alkane dimers.



Scheme 1.

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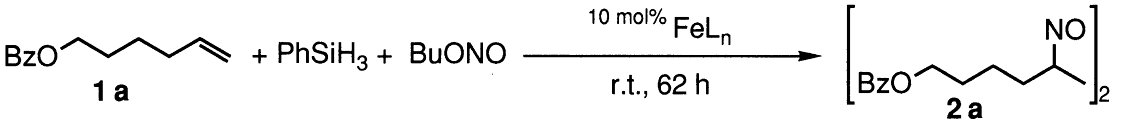
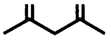
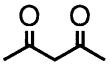
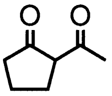
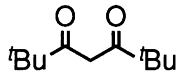
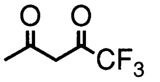
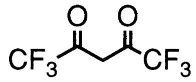
In this communication, we would like to report a novel method for the preparation of nitroso alkane dimers from terminal and 1,2-disubstituted olefins with butyl nitrite and phenylsilane under the catalytic action of a tris(1,3-diketonato)iron(III) complex (Scheme 1).

Table 1. Nitrosation of 5-Hexenyl Benzoate (**1a**) Catalyzed by Various Metal Complexes[a]

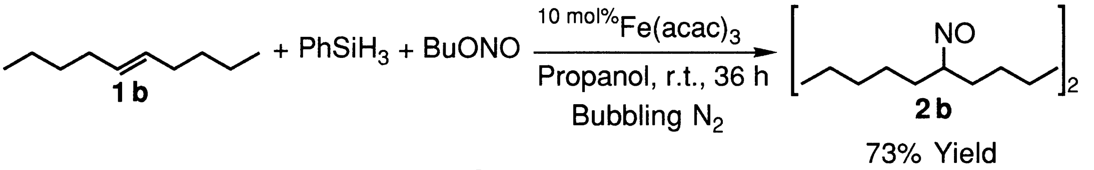


Bz=PhCO-

Entry	FeL_n	Ligand(HL)	Yield/%[b]
1	$Fe(acac)_3$	 (Hacac)	51
2	$Fe(acac)_2$	 (Hacac)	44
3	$Fe(acp)_3$	 (Hacp)	49
4	$Fe(dpm)_3$	 (Hdpm)	46
5	$Fe(tfa)_3$	 (Htfa)	15
6	$Fe(hfa)_3$	 (Hhfa)	12

a) Reaction conditions; 5-hexenyl benzoate (**1a**) 0.5 mmol, FeL_n 0.05 mmol, butyl nitrite 1.5 mmol, phenylsilane 1.5 mmol, in 2-propanol 2.5 ml, under an argon atmosphere, room temperature, 62 h. b) Isolated yield.

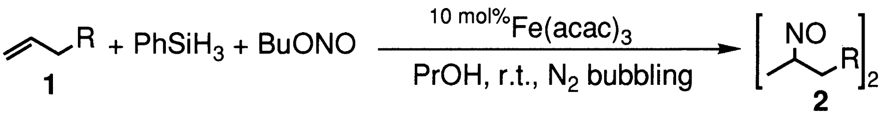
First, the catalytic activity of $Fe(acac)_3$ and bis(acetylacetonato)iron(II) ($Fe(acac)_2$) in the nitrosation of olefins was examined by adopting the reaction of 5-hexenyl benzoate (**1a**) (0.5 mmol) with butyl nitrite[5)] (1.5 mmol) and phenylsilane (1.5 mmol) in 2-propanol (2.5 ml) in the presence of an iron complex (0.05 mmol) at room temperature under an argon atmosphere for 62 h. It was found that the both complexes showed the high catalytic activity (see Entries 1 and 2 in Table 1), and in the case of $Fe(acac)_3$ particularly, the desired product, 5-nitrosohexyl benzoate dimer (**2a**), was obtained in a 51% yield (Entry 1). Furthermore, the effect of ligands of the iron(III) complexes on the catalytic activity was examined (see Entries 3-6 in Table 1). Consequently, the iron(III) complex coordinated 1,3-diketone-type ligands with electron-donating groups such as tris(2-acetylcyclopentanato)iron(III) ($Fe(acp)_3$) and tris(2,2,6,6-tetramethyl-3,5-heptanedionato)iron(III) ($Fe(dpm)_3$) showed the catalytic activity as high as $Fe(acac)_3$ (Entries 3 and 4). On the contrary, the yields of 5-nitrosohexyl benzoate dimer (**2a**) were only 15% and 12% respectively when tris(1,1,1-trifluoro-2,4-pentanedionato)iron(III) ($Fe(tfa)_3$) or tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)iron(III) ($Fe(hfa)_3$) was used as a catalyst (Entries 5 and 6).

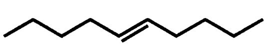
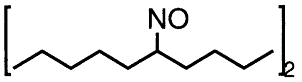
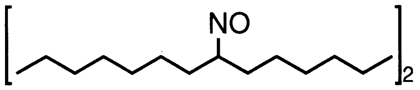
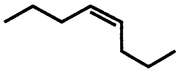
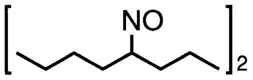
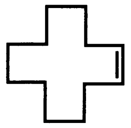
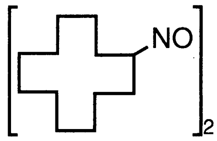
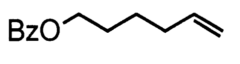
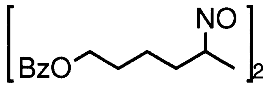
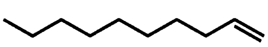
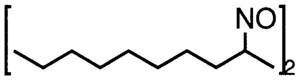
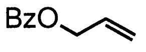
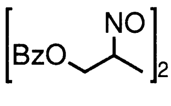
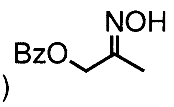


Scheme 2.

Next, various reaction conditions were examined in order to improve the yield in the nitrosation. When the nitrosation of 5-decene (**1b**) was carried out with bubbling N_2, the yield of the corresponding nitroso alkane dimer **2b** was raised up to 73% from 54% (Scheme 2). It is considered that the removal of nitrogen monoxide generated by the gradual decomposition of butyl nitrite from the reaction mixture by bubbling N_2 suppressed the deactivation of the catalyst by nitrogen monoxide and the yield of **2b** was improved. Actually, no nitrosation proceeded at all under nitrogen monoxide atmosphere.[6]

Table 2. Nitrosation of Various Olefins with BuONO and $PhSiH_3$ Catalyzed by $Fe(acac)_3$[a]



Entry	Substrate		Product[b]		Yield/%[c]
1		**1b**		**2b**	73
2		**1c**		**2c**	62
3		**1d**		**2d**	52
4		**1e**		**2e**	48
5		**1a**		**2a**	64
6		**1f**		**2f**	58
7		**1g**	 **2g** +  (1 : 2)	**3**	69

a) Reaction conditions; substrate 0.5 mmol, $Fe(acac)_3$ 0.05 mmol, butyl nitrite 3.0 mmol, phenylsilane 1.0 mmol, propanol 5 ml, bubbling N_2 (1.5 ml/min), room temperature, 62 h.
b) Satisfactry NMR and IR spectra were obtained. c) Isolated yield.

The above procedure was successfully applied to various olefins. As shown in Table 2, 1,2-disubstituted and terminal olefins were converted into the corresponding nitroso alkane dimers in fairly good yields. Thus, in the cases of (E)-5-decene (**1b**) and (E)-7-tetradecene (**1c**), the reactions took place smoothly and the nitroso alkane dimers **2b** and **2c** were obtained in 73% and 62% yields, respectively (Entries 1 and 2). And the nitrosations of (Z)-octene (**1d**) and cyclododecene (**1e**) also gave the desired products **2d** and **2e** in moderate yields (Entries 3 and 4), while in all cases of terminal olefins, the nitroso alkane dimers having a nitroso function onto the more substituted carbon atom were obtained selectively (Entries 5-7). Also, the nitrosation of allyl benzoate (**1g**) afforded 1-benzoyloxy-2-propanone oxime (**3**) together with the corresponding nitroso alkane dimer **2g** in a 69% total yield (**3**/**2g**=2/1) (Entry 7). On the other hand, in the case of trisubstituted olefin such as citronellyl benzoate, no nitrosated product was obtained at all in spite of the consumption of olefin in a 60% conversion.

A typical procedure is described for the nitrosation of 5-decene (**1b**) : To a solution of 5-decene (**1b**) (70 mg, 0.5 mmol), phenylsilane (108 mg, 1.0 mmol), and butyl nitrite (309 mg, 3.0 mmol) in propanol (5 ml) was added tris(acetylacetonato)iron(III) ($Fe(acac)_3$) (18 mg, 0.05 mmol). After stirring for 47 h at room temperature with bubbling N_2 (1.5 ml/min), the volatile materials were evaporated under reduced pressure. And the residue was purified by silica gel TLC (hexane-EtOAc, 9:1) to afford 5-nitrosodecane dimer (**2b**) (63 mg, 73%). ^1H-NMR ($CDCl_3$) δ=0.87 (12H, t, *J*=6 Hz), 1.26 (20 H, m), 1.60 (4H, m), 1.87 (4H, m), 5.44 (2H,m); IR ($CHCl_3$) 2958, 2930, 2862, 1466, 1391, 1226, and 1182 cm^{-1}; FD-MS m/z 342 (M^+).

It is noted that various terminal and 1,2-disubstituted olefins react with butyl nitrite and phenylsilane in the presence of a tris(1,3-diketonato)iron(III) complex as a catalyst at room temperature to give the corresponding nitroso alkane dimers in fairly good yields. Thus, the present nitrosation provides a novel method for the formation of nitroso alkane dimers from olefins.

References

1) K. B. Sharpless, A. O. Chong, and K. Oshima, *J. Org. Chem.*, **41**, 177 (1976).
2) T. Okamoto, K. Kobayashi, S. Oka, and S. Tanimoto, *J. Org. Chem.*, **52**, 5089 (1987); T. Okamoto, K. Kobayashi, S. Oka, and S. Tanimoto, *ibid.*, **53**, 4897 (1988).
3) K. Kato and T. Mukaiyama, *Chem. Lett.*, **1990**, 1395.
4) K. Kato and T. Mukaiyama, *Chem. Lett.*, **1990**, 1917; K. Kato and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, **64**, 2948 (1991).
5) Butyl nitrite was distilled before use.
6) A mixture of 5-decene (**1b**) (0.5 mmol), butyl nitrite (3.0 mmol), phenylsilane (1.0 mmol), and $Fe(acac)_3$ (0.05 mmol) in propanol (2.5 ml) was stirred under a mixed gas of NO and N_2 (1:1). Even after stirring for 38 h, no 5-nitrosodecane dimer (**2b**) was obtained at all and 80% of 5-decene (**1b**) was recovered.

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